CLAIMS

1. A method of forming a hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment, said method comprising:

- applying onto the substrate a particle mixture consisting of:
  - (a) 60 to 99 weight%, in particular 70 to 95 weight% such as 75 to 85 weight%, of: hematite (Fe_2O_3), or hematite and:
    - (1) iron metal (Fe) with a weight ratio Fe/Fe_2O_3 of preferably no more than 2, in particular in the range from 0.6 to 1.3;
    - (2) ferrous oxide (FeO) with a weight ratio FeO/Fe_2O_3 of preferably no more than 2.5, in particular in the range from 0.7 to 1.7; or
    - (3) iron metal (Fe) and ferrous oxide (FeO), with weight ratios Fe/Fe_2O_3 and FeO/Fe_2O_3 that are in pro rata with the ratios of (1) and (2);
  - (b) 1 to 25 weight%, in particular 5 to 20 weight% such as 8 to 15 weight%, of nitride and/or carbide particles; and
  - (c) 0 to 15 weight%, in particular 5 to 15 weight%, of one or more further constituents that consist of at least one metal or metal oxide or a heat-convertible precursor thereof;

and

- consolidating the hematite by heat treating the particle mixture to:
  - (1) oxidise iron metal (Fe) when present into ferrous oxide (FeO);
  - (2) sinter the hematite (Fe_2O_3) to form a porous sintered hematite matrix; and
  - (3) oxidise the ferrous oxide (FeO), when present in the particle mixture as such and/or upon oxidation of said iron metal (Fe), into hematite (Fe_2O_3) so as to fill the sintered hematite matrix,

  and form the protective layer that is made of a microporous sintered hematite matrix in which the nitride and/or carbide particles are embedded and which

contains, when present, said one or more further constituents.

2. The method of claim 1, wherein said nitride and/or carbide particles are selected from boron nitride, aluminium nitride, silicon nitride, silicon carbide, tungsten carbide and zirconium carbide, and mixtures thereof.

3. The method of claim 1 or 2, wherein said one or more further constituents are selected from oxides of titanium, yttrium, ytterbium, tantalum, manganese, zinc, zirconium, cerium and nickel and/or heat-convertible precursors thereof.

4. The method of claim 3, wherein the selected further constituent(s) of claim 3 is/are present in the protective layer in a total amount of 1 to 15 weight%, preferably 5 to 12 weight%.

5. The method of any preceding claim, wherein said one or more further constituents are selected from metallic Cu, Ag, Pd, Pt, Co, Cr, Al, Ga, Ge, Hf, In, Ir, Mo, Mn, Nb, Re, Rh, Ru, Se, Si, Sn, Ti, V, W, Li, Ca, Ce and Nb and oxides thereof, and/or heat-convertible precursors thereof.

6. The method of claim 5, wherein the selected further constituent(s) of claim 5, in particular copper and/or copper oxide, is/are present in a total amount of 0.5 to 15 weight%, preferably from 0.5 to 5 weight, in particular from 1 to 3 weight%.

7. The method of any preceding claim, wherein the particle mixture is made of particles that are smaller than 75 micron, preferably smaller than 50 micron, in particular from 5 to 45 micron.

8. The method of any preceding claim, wherein the substrate is metallic, a ceramic, a cermet or metallic with an integral oxide layer.

9. The method of any preceding claim, wherein the substrate comprises at least one metal selected from

chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium.

10. The method of claim 9, wherein the substrate comprises an alloy of iron, in particular an iron-nickel alloy optionally containing at least one further element selected from cobalt, copper, aluminium, yttrium, manganese, silicon and carbon.

11. The method of any preceding claim, comprising oxidising the surface of a metallic substrate to form an integral anchorage layer thereon to which the protective layer is bonded by sintering during heat treatment, in particular an integral layer containing an oxide of iron and/or another metal, such as nickel, that is sintered during heat treatment with iron oxide from the particle mixture.

12. The method of any preceding claim, wherein the particle mixture is applied in a slurry onto the substrate.

13. The method of claim 12, wherein the slurry comprises an organic binder, in particular a binder selected from polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, hexanol, butyl benzyl phthalate and ammonium polymethacrylate.

14. The method of claim 12 or 13, wherein the slurry comprises an inorganic binder, in particular a colloid, such as a colloid selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of colloids; and/or an inorganic polymer, such as a polymer selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide,

gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of inorganic polymers.

15. The method of claim 14, wherein the inorganic binder is sintered during the heat treatment with an oxide of an anchorage layer which is integral with the substrate to bind the protective layer to the substrate.

16. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment at a temperature in the range from 800° to 1400°C, in particular from 850° to 1150°C.

17. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment for 1 to 48 hours, in particular for 5 to 24 hours.

18. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment in an atmosphere containing 10 to 100 mol% O_2.

19. The method of any preceding claim for manufacturing a component of a metal electrowinning cell, in particular an aluminium electrowinning cell, which during use is exposed to molten electrolyte and/or cell fumes and protected therefrom by said protective layer.

20. The method of claim 19 for manufacturing a current carrying anodic component, in particular an active anode structure or an anode stem.

21. The method of claim 19 for manufacturing a cover.

22. The method of any one of claims 19 to 21, comprising consolidating the particle mixture to form the protective layer by heat treating the cell component over the cell.

23. A method of electrowinning a metal, such as aluminium, comprising manufacturing a current-carrying anodic component protected by said protective layer as

defined in claim 20, installing the anodic component in a molten electrolyte containing a dissolved salt of the metal to electrowin such as alumina, and passing an electrolysis current from the anodic component to a facing cathode in the molten electrolyte to evolve oxygen anodically and produce the metal cathodically.

24. The method of claim 23, wherein the electrolyte is a fluoride-based molten electrolyte, in particular containing fluorides of aluminium and sodium.

25. The method of claim 23 or 24, comprising maintaining the electrolyte at a temperature in the range from 800° to 960°C, in particular from 880° to 940°C.

26. The method of any one of claims 23 to 25, comprising maintaining in the electrolyte, particularly adjacent the anodic component, an alumina concentration which is at or close to saturation.

27. The method of any one of claims 23 to 26, comprising maintaining an amount of iron species in the electrolyte to inhibit dissolution of the protective layer of the anodic component.

28. A method of electrowinning a metal, such as aluminium, comprising manufacturing a cover protected by said protective layer as defined in claim 21, placing the cover over a metal electrowinning cell trough containing a molten electrolyte in which a salt of the metal to electrowin is dissolved, passing an electrolysis current in the molten electrolyte to evolve oxygen anodically and the metal cathodically, and confining electrolyte vapours and evolved oxygen within the cell trough by means of the protective layer of the cover.

29. A hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment, producible by the method of any one of claims 1 to 22, which is microporous and at least substantially crack-free and contains nitride and/or carbide particles.

30. A cell for the electrowinning of a metal, such as aluminium, having at least one component that comprises a metal-based substrate covered with a hematite-containing protective layer as defined in claim 29.

31. A method of forming a hematite-containing body for use in a high temperature oxidising and/or corrosive environment, said method comprising:

- providing a particle mixture consisting of:
  - (a) 60 to 99 weight%, in particular 70 to 95 weight% such as 75 to 85 weight%, of: hematite (Fe_2O_3), or hematite and:
    - (1) iron metal (Fe) with a weight ratio Fe/Fe_2O_3 of preferably no more than 2, in particular in the range from 0.6 to 1.3;
    - (2) ferrous oxide (FeO) with a weight ratio FeO/Fe_2O_3 of preferably no more than 2.5, in particular in the range from 0.7 to 1.7; or
    - (3) iron metal (Fe) and ferrous oxide (FeO), with weight ratios Fe/Fe_2O_3 and FeO/Fe_2O_3 that are in pro rata with the ratios of (1) and (2);
  - (b) 1 to 25 weight%, in particular 5 to 20 weight% such as 8 to 15 weight%, of nitride and/or carbide particles; and
  - (c) 0 to 15 weight%, in particular 5 to 15 weight%, of one or more further constituents that consist of at least one metal or metal oxide or a heat-convertible precursor thereof;
- shaping the particle mixture into the body;

and

- consolidating the hematite by heat treating the particle mixture to:
  - (1) oxidise iron metal (Fe) when present into ferrous oxide (FeO);
  - (2) sinter the hematite (Fe_2O_3) to form a porous sintered hematite matrix; and
  - (3) oxidise the ferrous oxide (FeO), when present in the particle mixture as such and/or upon oxidation of said iron metal (Fe), into hematite (Fe_2O_3) so as to fill the sintered hematite matrix,

and form the hematite-containing body that is made of a microporous sintered hematite matrix in which the

nitride and/or carbide particles are embedded and which contains, when present, said one or more further constituents.

32. The method of claim 31, incorporating any of the features of claims 2 to 7 and/or wherein the particle mixture is provided in a slurry and consolidated as defined in any one of claims 13, 14, 16, 17 or 18.

33. The method of claim 31 or 32, for manufacturing a component as defined in claims 19 to 21.